PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-199524

(43)Date of publication of application : 31.07.1998

(51)Int.Cl. H01M 4/38
H01M 4/02
H01M 10/40

(21)Application number : 09-006223

(22)Date of filing : 17.01.1997

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(54) NON-AQUEOUS ELECTROLYTE BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To enable an excellent charging/discharging property and a high safety under a high potential and a high energy density by employing, as a negative active material, a foreign semiconductor having its conductivity capable of starting/releasing lithium reversely in an operational range in which any change in a crystal system in volume is small at the time of lithium starting/relating in the case of charging/ discharging time.

SOLUTION: An extrinsic semiconductor provides suitability of a high electron conductivity material to be set in an alloy with lithium and particularly a foreign semiconductor whose electron conductivity is higher than 10-5Scm-1 at a normal temperature is excellent in its charging/discharging characteristics. Namely, lithium and silicon alloy is well known but silicon is originally a intrinsic semiconductor with low electron conductivity and its characteristics are poor as a battery negative acute material. However, extrinsic semiconductors such as p-type, n-type, p-n junction semiconductor with doped impurity, etc., particularly in p-type and n-type semiconductor, such a one of good electron conductivity at a high impurity concentration, and such one as having p-n junction at low impurity concentration with low electric resistance for forward current are excellent in both charging/discharging characteristics as negative active substance.

LEGAL STATUS

[Date of request for examination] 29.09.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]	
[Patent number]	3620559
[Date of registration]	26.11.2004
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

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CLAIMS

[Claim(s)]
[Claim 1] The nonaqueous electrolyte cell by which the quality of a main truss product of a negative-electrode active material is characterized by consisting of an extrinsic semiconductor.
[Claim 2] The nonaqueous electrolyte cell according to claim 1 by which the quality of a main truss product of said extrinsic semiconductor is Si or germanium, and at least one or more kinds of impurities are doped by this Si or germanium.
[Claim 3] The nonaqueous electrolyte cell according to claim 2 said whose impurity is at least one or more sorts of the element of an IIIb group, an IVb group, and Vb group.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the negative-electrode active material in more detail about a nonaqueous electrolyte cell.
[0002]
[Description of the Prior Art] Although it was more typical than before as a negative-electrode active material for nonaqueous electrolyte cells to have used a lithium, there was a problem in respect of a cycle life for an arborescence deposit (dendrite) of the lithium generated at the time of charge. Moreover, this dendrite penetrates a separator, and an internal short circuit is caused or it causes ignition.
[0003] Moreover, the lithium alloy was also used in order to prevent the dendrite generated at the time of the above charge, but when the charge became large, there were problems, such as fine pulverization of a negative electrode and omission of a negative-electrode active material.
[0004] The cell which uses a carbon material for a negative electrode for current, reinforcement, and safety attracts attention, and is put in practical use in part. However, the carbon material used for a negative electrode had a problem of an internal short circuit or decline in charging efficiency at the time of boosting charge. Generally, since the dope potential of the lithium to a carbon material was close to 0V, potential might become less than [0V] and these carbon materials might deposit the lithium on the electrode, when boosting charge was performed. Therefore, the internal short circuit of a cel is caused or it becomes the cause that discharge effectiveness falls. Moreover, although the improvement with such a carbon material remarkable in respect of a cycle life is made, since the consistency is comparatively small, the capacity per volume will become low. That is, this carbon material is still insufficient from the point of a high energy consistency. Moreover, initial charge-and-discharge effectiveness falls about what needs to form a coat on carbon, and since quantity of electricity used for this coat formation is irreversible, it leads to the capacity lowering for that quantity of electricity.
[0005] On the other hand, multiple oxide Lix Si1-y My Oz (JP,7-230800,A) containing silicon and a lithium and using amorphous chalcogen compound M1 M2 p M4 q (JP,7-288123,A) are advocated as negative-electrode active materials other than a metal lithium, a lithium alloy, or a carbon material, and it is improved in respect of high capacity and a high energy consistency.
[0006] However, since the own electrical conductivity of an active material of the above multiple oxides was low, the problem was in boosting charge and a load characteristic. Although addition of an electric conduction agent is tried in order to solve this problem, when a carbon material with a low consistency is used as an electric conduction agent, the capacity per volume will fall. Furthermore, by adding an electric conduction agent, when boosting charge was performed, current concentration took place selectively, and the deposit of a lithium was observed from the electric conduction agent. Therefore, the internal short circuit of a cel might be caused and charge-and-discharge effectiveness might be reduced.
[0007] Moreover, since a multiple oxide etc. was considered that a reaction with a lithium advances through reduction of oxide since the ingredient itself is oxide, especially the irreversible reduction in the first stage might take place, and initial charge-and-discharge effectiveness might become low.
[0008] Under such a situation, by the further high capacity and the high energy consistency, a cycle life is long and development of the safe negative-electrode ingredient for nonaqueous electrolyte cells is desired.
[0009]
[Problem(s) to be Solved by the Invention] That is, although it is advantageous in respect of high tension and safety when a problem has an advantage as high tension, and high capacity and a high energy consistency on the cycle engine performance of a certain thing, or safety when using the alloy of a lithium metal, or a lithium and a metal as a negative electrode, and using a carbon material, the field of high capacity and a high energy consistency is inadequate. Furthermore, when using an oxide negative electrode,

the point of high capacity and a high energy consistency is not satisfactory in respect of high tension, a charge-and-discharge effectiveness property, and a cycle life or safety, although it seems that it is improved.

[0010] For this reason, in order to show the outstanding charge-and-discharge cycle property and to obtain a rechargeable battery with high safety by high tension and the high energy consistency, there are few change and the volume changes of crystal system in the case of occlusion bleedoff of the lithium at the time of charge and discharge, and it is expected development of the compound which is an operating space near lithium potential as much as possible, and has reversibly the conductivity which can occlusion emit a lithium.

[0011]

[Means for Solving the Problem] It is characterized by making this invention in view of the above-mentioned trouble, and consisting of extrinsic semiconductors, such as a semi-conductor with which the ideal negative-electrode active material used for a nonaqueous electrolyte cell is proposed, and the quality of a main truss product of a negative-electrode active material has a p type semiconductor, a n-type semiconductor, and p-n junction.

[0012] Furthermore, the quality of a main truss product of the extrinsic semiconductor mentioned above is Si or germanium, at least one or more kinds of impurities are doped by them, and the impurity in the quality of a main truss product of said extrinsic semiconductor is characterized by being the element of IIIb groups, such as P, aluminum, As, Sb, B, Ga, and In, IV group, and Vb group.

[0013] previously -- as the alloy of a lithium and silicon -- Binary Alloy Phase it is in Diagrams (p2465) -- as -- Li22Si5 up to -- alloying by presentation is known. Moreover, JP,5-74463,A has reported that a cycle property improves by using the single crystal of silicon for a negative electrode. However, when silicon was made to dope a lithium and it tried as like as negative-electrode material of the nonaqueous electrolyte cell for rapid charges and discharges, it turned out that a lithium deposits without a dope hardly taking place. Then, as a result of this invention persons' examining extrinsic semiconductors, such as a p type semiconductor which already has an impurity (dopant), a n-type semiconductor, and a semi-conductor which has p-n junction, it turned out that the occlusion of a lithium and bleedoff advance smoothly, without phenomena, such as breaking and impalpable-powder-izing of a crystal, and omission, happening. Furthermore, it turned out that this reaction advances with the potential very near lithium potential about 0.1V, the high capacity near geometric capacity is obtained, and it excels in reversibility.

[0014] Moreover, this extrinsic semiconductor was understood that what was excellent in electronic conduction nature is also suitable for alloying with a lithium. especially -- whenever [electronic conduction] -- ordinary temperature -- 10-5Scm- it turned out that the extrinsic semiconductor which is more than 1Scm-1 is excellent in a charge-and-discharge property preferably one or more. That is, although the alloy of a lithium and silicon was known, it was an intrinsic semiconductor originally, if silicon itself remained as it was, its electronic conduction nature was low, and the property as a cell negative-electrode ingredient was bad [itself]. Therefore, although it was the raw material which cannot be easily set as the object of research Extrinsic semiconductors, such as a p type semiconductor which doped the impurity, a n-type semiconductor, and a semi-conductor which has p-n junction, It sets especially to p mold and a n-type semiconductor. The good thing of electronic conduction nature which has high high impurity concentration Moreover, even if high impurity concentration was low, it found out that had p-n junction and what has low electric resistance was excellent in a charge-and-discharge property as [both] a negative-electrode active material to the current of the forward direction, and it resulted in this invention.

[0015]

[Embodiment of the Invention] Although it is desirable since the charge-and-discharge property which Si, germanium, GaAs, GaP, InSb, GaP, SiC, etc. were mentioned, among those was excellent about Si and especially germanium as a semiconductor material said here is acquired, it is not limited to these. Moreover, although it is desirable since the charge-and-discharge property which a single crystal, polycrystal, and amorphous ** were mentioned about the crystal system, among those was excellent about especially the single crystal is acquired, it is not limited to these.

[0016] Furthermore, although the impurity said here can serve as a donor atom and an acceptor atom among all the elements of the periodic table and is the element of IIIb groups, such as P, aluminum, As, Sb, B, Ga, In, and Sn, an IVb group, and Vb group preferably, it is not limited to these.

[0017] As the doping approach of the above-mentioned impurity, a CZ process (Czochralski method or Czochralski method), FZ (floating zone method), and when especially p-n junction makes, although an alloying method, a diffusion method, ion-implantation, the epitaxial method, etc. are mentioned, it is not limited to these.

[0018] About the concentration of impurity addition, it is usually the silicon atom 107. An individual to

106 Although it is the rate of a donor atom or one acceptor atom, desirable high-concentration doping is suitable for the individual, and it is the silicon atom 104. It is desirable to an individual that they are the rate of a donor atom or one acceptor atom or the high concentration beyond it.

[0019] The extrinsic semiconductor used for this invention has the desirable fine particles which are the veneer or average grain size of 0.1-100 micrometers of the shape of a wafer whose thickness is 0.1-500 micrometers. A grinder and a classifier are used, in order to use a diamond cutter in order to obtain the wafer-like veneer and to obtain fine particles, when acquiring a predetermined configuration. When obtaining fine particles, a mortar, a ball mill, a sand mill, a vibration ball mill, a planet ball mill, a jet mill, counter JIETOMIRU, a turning air-current mold jet mill, a screen, etc. are used. At the time of grinding, wet grinding which made organic solvents, such as water or a hexane, live together can also be used. As the classification approach, there is especially no definition and a screen, a pneumatic elutriation machine, etc. are used if needed in dry type and wet.

[0020] The organic compound which contains lithiums, such as a lithium metal, a lithium alloy, etc. a baking carbonaceous compound that can carry out occlusion bleedoff of a lithium ion or the lithium metal, a chalcogen compound, and methyl lithium, as a negative-electrode ingredient which can be combined and can be used for this invention is mentioned. Moreover, it is also possible by using together the organic compound containing a lithium metal, a lithium alloy, and a lithium to insert a lithium in the extrinsic semiconductor used for this invention inside a cell.

[0021] the case where the extrinsic semiconductor of this invention is used as powder -- an electrode -- an electric conduction agent, a binder, a filler, etc. can be added as a mixture. If it is the electronic conduction nature ingredient which does not have an adverse effect on the cell engine performance as an electric conduction agent, it is good anything. Usually, conductive ingredients, such as natural graphites (flaky graphite, a scale-like graphite, earthy graphite, etc.), an artificial graphite, carbon black, acetylene black, KETCHIEN black, a carbon whisker, carbon fiber metallurgy group powder (copper, nickel, aluminum, silver, gold, etc.), a metal fiber, a metaled vacuum evaporationo object, and a conductive ceramic ingredient, can be included as one sort or those mixture. In these, concomitant use of a graphite, acetylene black, and KETCHIEN black is desirable. The addition has 1 - 50 desirable % of the weight, and its 2 - 30 % of the weight is especially desirable.

[0022] As a binder, a polymer, polysaccharide, etc. which have thermoplastic trees, such as tetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), sulfonation EPDM, styrene butadiene rubber (SBR), a fluororubber, and a KARUBO methoxy cellulose, and rubber elasticity can usually be used as one sort or two sorts or more of mixture. Moreover, as for a lithium and the binder which has the functional group which reacts, it is desirable like polysaccharide to methylate, for example and to carry out deactivation of the functional group. As the addition, 1 - 50 % of the weight is desirable, and 2 - 30 % of the weight is especially desirable.

[0023] If it is the ingredient which does not have an adverse effect on the cell engine performance as a filler, it is good anything. Usually, olefin system polymers, such as polypropylene and polyethylene, Aerosil, a zeolite, glass, carbon, etc. are used. The addition of a filler has 0 - 30 desirable % of the weight.

[0024] If it is the electronic conductor which does not do an adverse effect in the constituted cell as a charge collector of an electrode active material, it is good anything. For example, as an ingredient of a positive-electrode charge collector, besides aluminum, titanium, stainless steel, nickel, baking carbon, a conductive polymer, electrically conductive glass, etc., it is the object of an adhesive property, conductivity, and oxidation-resistant improvement, and the object which processed front faces, such as aluminum and copper, with carbon, nickel, titanium, silver, etc. can be used. As an ingredient of a negative-electrode charge collector, besides copper, stainless steel, nickel, aluminum, titanium, baking carbon, a conductive polymer, electrically conductive glass, an aluminum-Cd alloy, etc., it is the object of an adhesive property, conductivity, and oxidation-resistant improvement, and the object which processed front faces, such as copper, with carbon, nickel, titanium, silver, etc. can be used. About these ingredients, it is also possible to oxidize a front face. About these configurations, the shape of the shape of the shape of others and a film and a sheet and a network, punch or the configuration by which expanded one was carried out, a lath object, a porous body, a firing object, the organizer of a fiber group, etc. are used. [shape / of foil] Although especially definition is thin, an about 1-500-micrometer thing is used.

[0025] Thus, extrinsic semiconductors, such as a p type semiconductor obtained, a n-type semiconductor, and a semi-conductor which has p-n junction, are used as a negative-electrode active material. on the other hand -- as positive active material -- MnO2, MoO3, V2 O5, Lix CoO2, Lix NiO2, and Lix Mn 2O4 etc. -- a metallic oxide, and TiS2, MoS2 and NbSe3 etc. -- various kinds of matter in which absorption/emission is possible can be used for alkali-metal ion, such as intercalated graphite, such as a metal chalcogen ghost, the poly acene, poly para-phenylene, polypyrrole, and the poly aniline, and a conductive polymer, and an

anion.
[0026] the viewpoint of [when using especially extrinsic semiconductors, such as a p type semiconductor of this invention, a n-type semiconductor and a semi-conductor that has p-n junction as a negative-electrode active material] a high energy consistency to V2 -- O5, MnO2, Lix CoO2, Lix NiO2, and Lix Mn 2O4 etc. -- what has the electrode potential of 3-4V is desirable. especially -- Lix CoO2, Lix NiO2, and Lix Mn 2O4 etc. -- a lithium content transition-metals oxide is desirable.
[0027] Moreover, it is desirable to be able to use the organic electrolytic solution, a solid polymer electrolyte, an inorganic solid electrolyte, fused salt, etc., for example, and to use the organic electrolytic solution also in this as an electrolyte. As an organic solvent of this organic electrolytic solution, propylene carbonate, ethylene carbonate, Butylene carbonate, diethyl carbonate, dimethyl carbonate, Ester, such as methylethyl carbonate and gamma-butyrolactone Permutation tetrahydrofurans, such as a tetrahydrofuran and 2-methyl tetrahydrofuran, Dioxolane, diethylether, dimethoxyethane, diethoxy ethane, Ether, such as methoxyethoxy ethane, dimethyl sulfoxide, a sulfolane, a methyl sulfolane, an acetonitrile, methyl formate, methyl acetate, N-methyl pyrrolidone, dimethyl formamide, etc. are mentioned, and these can be used as independent or a mixed solvent. moreover -- as a supporting-electrolyte salt -- LiClO4, LiPF6, LiBF4, LiAsF6, LiCF3 SO3, and LiN (CF3 SO2)2 etc. -- it is mentioned. On the other hand, the object which melted the above supporting-electrolyte salts as a giant-molecule solid electrolyte into polymers, such as polyethylene oxide, the bridge formation object and poly FOSUFAZEN, and its bridge formation object, can be used. Furthermore, inorganic solid electrolytes, such as Li3 N and LiI, are also usable. That is, what is necessary is just nonaqueous electrolyte of lithium ion conductivity.
[0028] As a separator, the transmittance of ion is excellent and an insulating thin film with a mechanical strength can be used. The sheet built from organic solvent-proof nature and hydrophobicity from the polymer of olefin systems, such as polypropylene and polyethylene, a glass fiber, polyvinylidene fluoride, polytetrafluoroethylene, etc., a micropore film, and a nonwoven fabric are used. The aperture of a separator is a thing of the range generally used for a cell, for example, is 0.01-10 micrometers. Moreover, the same is said of the thickness, and it is the thing of the range generally used for a cell, for example, is 5-300 micrometers.
[0029] When using as a tabular wafer-like configuration in the extrinsic semiconductor of this invention, a conductive glue line can also be prepared between a charge collector and an active material in order to take current collection. A silver paste and carbon paste are usually used as electroconductive glue. Moreover, junction by the pewter or fused metal like silver solder is also possible by carrying out nickel plating of some crystals. Moreover, the configuration is freely processible with a diamond cutter and etching processing.
[0030] Although the reason such an outstanding charge-and-discharge property is acquired is not necessarily clear, it is considered as follows. That is, it can observe that an alloy with a lithium is possible for the crystal which has covalent bond, such as silicon, and the capacity is large. However, although the crystal which has covalent bond, such as silicon, is a semi-conductor, it is an intrinsic semiconductor. The electrical conductivity in the ordinary temperature to a low thing with comparatively large polarization at the time of charge and discharge as extrinsic semiconductors, such as a p type semiconductor, a n-type semiconductor, and a semi-conductor that has p-n junction The zerovalent lithium by which whenever [electronic conduction] improved when the crystal which has covalent bond, such as silicon, was used, and could carry out occlusion of the lithium ion as a zerovalent lithium easily, and could give the electron, and occlusion was carried out emits an electron, and is emitted as a lithium ion. That is, it is presumed that the electron flow inside a crystal makes occlusion bleedoff of a lithium ion easy. Furthermore, it is thought that this crystal itself has covalent bond, it is dramatically firm since it is the face centered cubic structure as a diamond with that same structure, it follows in footsteps of dilatation contraction in connection with occlusion bleedoff of a lithium, and an active material's own detailed-izing or omission are not seen, but it is improving the reversibility of charge and discharge.
[0031] The negative-electrode active material which makes extrinsic semiconductors, such as a p type semiconductor of this invention, a n-type semiconductor, and a semi-conductor that has p-n junction, the quality of a main truss product Occlusion bleedoff of the lithium ion can be carried out in 0-2V at least to a metal lithium into nonaqueous electrolyte. Moreover, it can use as a negative electrode of the rechargeable battery which was excellent in the charge-and-discharge property in which a cycle is possible by suppressing the fine pulverization at the time of the charge and discharge looked at by the usual alloy, and partial isolation of a negative-electrode active material, and using such a negative-electrode active material as an electrode material from a semiconducting crystal being firm. Especially, the dope of a high-concentration impurity, and when the electronic conduction nature inside a crystal improves by having p-n junction, alloying of silicon and a lithium is made smooth and the rate property of charge and discharge

improves. Furthermore, since negative-electrode potential is close to lithium potential and low, the electrical potential difference as a cell turns into high tension, and since the capacity is large, a high energy consistency is attained.

[0032]

[Example] Hereafter, the example of this invention is explained.

(Example 1) By the diffusion method, it is the silicon atom 104. They are (a) and the silicon atom 104 about the silicon single crystal which is the n-type semiconductor doped at a rate of one P atom to the individual. They are (b) and the silicon atom 104 about the silicon single crystal which is the p type semiconductor doped at a rate of one B atom to the individual. It dopes at a rate of P and one B atom to an individual, and the silicon single crystal which is the semi-conductor in which p-n junction be formed be set to (c). It started in 5mm 0.3mm[in thickness] x long, and 5mm wide magnitude, and weight was measured. This specific resistance was [33Scm-1 and the p type semiconductor of the n-type semiconductor] 20Scm-1. Next, it put in two 10mm long and 10mm wide nickel mesh, and the wire was used as the installation test electrode. The following actuation was performed in dry air, and after all ingredients fully dried beforehand, they were used. Two things which stuck the metal lithium of suitable magnitude by pressure on the nickel plate were produced, and it considered as the counter electrode and the potential reference pole. It is LiClO4 in a beaker. It was immersed into the electrolytic solution and three electrodes which used as the electrolytic solution the propylene carbonate solution which dissolved in the concentration of one mol/l., and were produced above, i.e., test electrodes, the counter electrode, and the potential reference pole were used as the 3 terminal cel. The charge and discharge test was performed using this unipolar ability trial cel. The capacity test was performed in this cel about the range whose potentials of a trial pole [as opposed to a sink and a potential reference pole for 1mA current] are 0.00-2.00V.

(Example 1 of a comparison) The silicon single crystal (d) was cut down as a semi-conductor which does not contain an impurity in 5mm 0.3mm[in thickness] x long, and 5mm wide magnitude, and weight was measured. This specific resistance was 10-6Scm-1. Except this, the unipolar ability trial cel was produced like the above-mentioned example 1, and the same capacity test was performed.

[0033] Thus, the capacity test of the produced unipolar ability trial cel was performed. Silicon single crystal (a) The unipolar ability trial cel using - (d) is made into each cel (A) - (D). Cel (A) Although occlusion bleedoff of a lithium was checked about - (C), about a cel (D), occlusion bleedoff of a lithium was hardly completed, but the deposit of a lithium was observed. The capacity of the first stage at this time and the capacity of 10 cycle eye were shown in a table 1. About the negative electrode using the extrinsic semiconductor which doped the impurity which is this invention, it excels in charge-and-discharge cycle nature, and it turns out that it is high capacity so that clearly from this result.

[0034]

[A table 1]

単極性能試験セル	1サイクル(Ah/g)		10サイクル(Ah/g)	
	充電容量	放電容量	充電容量	放電容量
(A)	1. 9	1. 5	1. 5	1. 5
(B)	1. 9	1. 5	1. 5	1. 5
(C)	2. 0	1. 6	1. 6	1. 6
(D)	0. 1	0. 0	0. 0	0. 0

[0035] (Example 2) It is the silicon atom 104 as the silicon single crystal (a) used in the example 1, (b), and a n-type semiconductor. Lessons was taken for the silicon polycrystal which doped the silicon polycrystal doped at a rate of one P atom to the individual at a rate of one B atom in 104 silicon atoms as (e) and a p type semiconductor from (f), the mortar ground, and the coin mold lithium secondary battery was made as an experiment as follows using this negative-electrode active material. A negative-electrode active material, acetylene black, and polytetrafluoroethylene powder were mixed by the weight ratio 85:10:5,

toluene was added, and it kneaded enough. This was fabricated with a thickness of 0.3mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, it heat-treated at 200 degrees C under reduced pressure for 15 hours, and the negative electrode 2 was obtained. The negative electrode 2 was stuck by pressure and used for the negative-electrode can 5 to which the negative-electrode charge collector 7 was attached.

[0036] A positive electrode 1 is LiCoO2 as positive active material. Acetylene black and polytetrafluoroethylene powder were mixed by the weight ratio 85:10:5, toluene was added, and it kneaded enough. This was fabricated with a thickness of 0.8mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, it heat-treated at 200 degrees C under reduced pressure for 15 hours, and the positive electrode 1 was obtained. The positive electrode 1 was stuck by pressure and used for the positive-electrode can 4 to which the positive-electrode charge collector 6 was attached. It is LiPF6 to the partially aromatic solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate. The fine porous membrane made from polypropylene was used for the separator 3 using the electrolytic solution which dissolved in the concentration of one mol/l. The coin mold lithium cell with a diameter [of 20mm] and a thickness of 1.6mm was produced using the above-mentioned positive electrode, a negative electrode, the electrolytic solution, and a separator. The cell using this silicon single crystal (a) and (b) is set to A1 and B1, respectively, and the cell using silicon polycrystal (e) and (f) is set to E1 and F1, respectively. In addition, the sectional view of the coin mold lithium cell of this invention is shown in drawing 1 .

[0037] (Example 2 of a comparison) The aluminium powder was used instead of single crystal silicon, and the cell was produced like the example 2 except it. The obtained cell is set to G1.

[0038] (Example 3) The cell was produced like the example 2 except it, using as a negative electrode what coated the thickness of 0.1mm with the amorphous silicon, and poured in P and 1018 B per cubic centimeter with ion-implantation on the copper charge collector, respectively. The obtained cell is set to H1 and I1.

[0039] (Example 4) single crystal germanium powder is used instead of single crystal silicon, and epitaxial -- law -- germanium atom 104 the germanium single crystal which is the n-type semiconductor doped at a rate of one As atom to the individual -- (j) and germanium atom 104 The germanium single crystal which is the p type semiconductor doped at a rate of one In atom to the individual was set to (k), and the cell was produced like the example 2 except having used these single crystals for the negative electrode. The obtained cell is set to J1 and K1.

[0040] Thus, the charge-and-discharge cycle trial was performed using the produced cells A1, B1, E1, F1, G1, H1, I1, J1, and K1. The test condition was set to 3mA of charging currents, charge termination electrical-potential-difference 4.2V, 3mA of discharge currents, and discharge-final-voltage 3.0V. The result of the charge and discharge test of the these-produced cell is shown in a table 2.

[0041]

[A table 2]

電池	1サイクル(mAh)		10サイクル(mAh)	
	充電容量	放電容量	充電容量	放電容量
A1	65	63	62	62
B1	64	62	62	62
E1	63	61	55	54
F1	63	60	55	54
G1	65	62	30	28
H1	46	45	44	44
I1	46	45	44	44
J1	65	63	62	62
K1	65	63	62	62

[0042] As shown in a table 1, the cells A1, B1, E1, F1, H1, I1, J1, and K1 by this invention were excellent in the charge-and-discharge property compared with the comparison cell G1, and its capacity reduction after 10 cycles was small to the pan. Moreover, the comparison of A1, B1, and E1 and F1 shows that the cycle property of a single crystal semiconductor is superior to a polycrystal semi-conductor. Although it is not clear about this reason, it thinks as follows. A polycrystal semi-conductor is a set of the lump of many small crystals, and a grain boundary exists between crystals. these ingredients -- a ** lithium -- occlusion -- in emitting, the volume change of a crystal arises. That is, a crack goes into a grain boundary part in connection with this volume change, and it is thought that electronic isolation of an active material and impalpable powder-ization arise and cycle degradation takes place. Although capacity fell a little, about H1 and J1 using an amorphous silicon, the cycle property is excellent. Moreover, in the single crystal of silicon and germanium, a difference was hardly looked at by the engine performance.

[0043] In the example, although mentioned about silicon and germanium as an extrinsic semiconductor, the same effectiveness was checked about other extrinsic semiconductors. In addition, this invention is not limited to the start raw material, the manufacture approach, a positive electrode, a negative electrode, an electrolyte, a separator, a cell configuration, etc. of the active material indicated by the above-mentioned example.

[0044]

[Effect of the Invention] Since this invention is constituted like ****, it is high tension, high capacity, and a high energy consistency, and the outstanding charge-and-discharge cycle property is shown, and a nonaqueous electrolyte cell with high safety can be offered.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] That is, although it is advantageous in respect of high tension and safety when a problem has an advantage as high tension, and high capacity and a high energy consistency on the cycle engine performance of a certain thing, or safety when using the alloy of a lithium metal, or a lithium and a metal as a negative electrode, and using a carbon material, the field of high capacity and a high energy consistency is inadequate. Furthermore, when using an oxide negative electrode, the point of high capacity and a high energy consistency is not satisfactory in respect of high tension, a charge-and-discharge effectiveness property, and a cycle life or safety, although it seems that it is improved.
[0010] For this reason, in order to show the outstanding charge-and-discharge cycle property and to obtain a rechargeable battery with high safety by high tension and the high energy consistency, there are few change and the volume changes of crystal system in the case of occlusion bleedoff of the lithium at the time of charge and discharge, and it is expected development of the compound which is an operating space near lithium potential as much as possible, and has reversibly the conductivity which can occlusion emit a lithium.

[Translation done.]

* NOTICES *

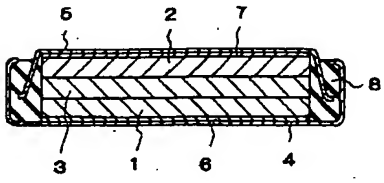
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the sectional view of the coin mold lithium cell of this invention.
[Description of Notations]
1 Positive Electrode
2 Negative Electrode
3 Separator
4 Positive-Electrode Can
5 Negative-Electrode Can
6 Positive-Electrode Charge Collector
7 Negative-Electrode Charge Collector
8 Insulating Packing

[Translation done.]

Drawing selection drawing 1



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(19)日本国特許庁（ＪＰ）　(12)公開特許公報（A）　(11)特許出願公開番号

特開平10－199524

(43)公開日　平成10年(1998)７月31日

(51)Int.Cl.[6]		識別記号	FI		
H01M	4/38		H01M	4/38	Z
	4/02			4/02	D
	10/40			10/40	Z

審査請求　未請求　請求項の数3　ＯＬ　（全７頁）

(21)出願番号　特願平9－6223

(22)出願日　平成９年(1997)１月17日

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(54)【発明の名称】　非水電解質電池

(57)【要約】

【目的】　高電圧、高容量、高エネルギー密度で、優れた充放電サイクル特性を示し、安全性の高い非水電解質電池を提供することを目的とする。

【構成】　負極活物質の主構成物質が、外来半導体からなる非水電解質電池とすることで、上記目的を達成できる。

【特許請求の範囲】

【請求項１】　負極活物質の主構成物質が、外来半導体からなることを特徴とする非水電解質電池。

【請求項２】　前記外来半導体の主構成物質が、Ｓｉ又はＧｅであり、該Ｓｉ又はＧｅには少なくとも一種類以上の不純物がドーピングされている請求項１記載の非水電解質電池。

【請求項３】　前記不純物が、ＩＩＩｂ族、ＩＶｂ族、Ｖｂ族の元素の少なくとも１種以上である請求項２記載の非水電解質電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は非水電解質電池に関するもので、さらに詳しくはその負極活物質に関するものである。

【０００２】

【従来の技術】従来より非水電解質電池用の負極活物質として、リチウムを用いることが代表的であったが、充電時に生成するリチウムの樹枝状析出（デンドライト）のため、サイクル寿命の点で問題があった。また、このデンドライトはセパレーターを貫通し内部短絡を引き起こしたり、発火の原因ともなっている。

【０００３】また、上記のような充電時に生成するデンドライトを防止する目的でリチウム合金も用いられたが、充電量が大きくなると負極の微細粉化や、負極活物質の脱落などの問題があった。

【０００４】現在、長寿命化及び安全性のために負極に炭素材料を用いる電池などが注目を集め一部実用化されている。しかしながら、負極に用いられる炭素材料は、急速充電時、内部短絡や充電効率の低下という問題があった。これらの炭素材料は一般的に、炭素材料へのリチウムのドープ電位が０Ｖに近いため、急速充電を行う場合、電位が０Ｖ以下になり電極上にリチウムを析出することがあった。そのため、セルの内部短絡を引き起こしたり、放電効率が低下する原因となる。また、このような炭素材料は、サイクル寿命の点でかなりの改善がなされているが、密度が比較的小さいため、体積当たりの容量が低くなってしまうことになる。つまり、この炭素材料は高エネルギー密度という点からは未だ不十分である。その上、炭素上に被膜を形成する必要があるものについては初期充放電効率が低下し、この被膜形成に使われる電気量は不可逆であるため、その電気量分の容量低下につながる。

【０００５】一方、金属リチウムやリチウム合金または炭素材料以外の負極活物質として、シリコンとリチウムを含有する複合酸化物$Li_xSi_{1-y}M_yO_z$（特開平７－２３０８００号）や、非晶質カルコゲン化合物$M^1M^2{}_pM^4{}_q$（特開平７－２８８１２３号）を用いることが提唱されており、高容量、高エネルギー密度の点で改善されている。

【０００６】しかしながら、上記のような複合酸化物は、活物質自身の電気伝導度が低いため、急速充電及び負荷特性に問題があった。この問題を解決する目的で導電剤の添加が試みられているが、密度の低い炭素材料を導電剤として用いると、体積当たりの容量が低下することになる。さらに、導電剤を添加することにより、急速充電を行うと部分的に電流集中が起こり、導電剤からリチウムの析出が観測された。そのため、セルの内部短絡を引き起こしたり、充放電効率を低下させることがあった。

【０００７】また、複合酸化物等は材料自身が酸化物であるため、酸化物の還元を経てリチウムとの反応が進行すると考えられるため、特に初期での不可逆的な還元が起こり、初期充放電効率が低くなることがあった。

【０００８】この様な状況下でさらなる高容量、高エネルギー密度で、サイクル寿命が長く、安全な非水電解質電池用負極材料の開発が望まれている。

【０００９】

【発明が解決しようとする課題】即ち、負極としてリチウム金属やリチウムと金属の合金を用いる場合は、高電圧や、高容量、高エネルギー密度としての利点はあるものの、サイクル性能や安全性の上で問題があり、炭素材料を用いる場合は、高電圧や、安全性の面で有利であるものの、高容量、高エネルギー密度の面で不十分である。さらに、酸化物負極を用いる場合は、高容量、高エネルギー密度の点は改善されているようであるが、高電圧、充放電効率特性、サイクル寿命や安全性の点では満足がいかないものである。

【００１０】このため、高電圧、高エネルギー密度で、優れた充放電サイクル特性を示し、安全性の高い二次電池を得るには、充放電時のリチウムの吸蔵放出の際に結晶系の変化や体積変化が少なく、できるだけリチウム電位に近い作動領域で、かつ可逆的にリチウムを吸蔵放出可能な導電性のある化合物の開発が望まれている。

【００１１】

【課題を解決するための手段】本発明は上記問題点に鑑みてなされたものであって、非水電解質電池に使用される理想的な負極活物質を提案するもので、負極活物質の主構成物質が、ｐ型半導体、ｎ型半導体、ｐ－ｎ接合を有する半導体等の外来半導体からなることを特徴とする。

【００１２】さらに、上記に挙げた外来半導体の主構成物質が、Ｓｉ又はＧｅであり、それらには少なくとも一種類以上の不純物がドーピングされており、前記外来半導体の主構成物質中の不純物が、Ｐ，Ａｌ，Ａｓ，Ｓｂ，Ｂ，Ｇａ，Ｉｎ等のＩＩＩｂ族、ＩＶ族、Ｖｂ族の元素であることを特徴とする。

【００１３】先に、リチウムとシリコンの合金としては Ｂｉｎａｒｙ　Ａｌｌｏｙ　Ｐｈａｓｅ　Ｄｉａｇｒａｍｓ（ｐ２４６５）にあるように、$Li_{22}Si_5$までの

組成で合金化することが知られている。また、特開平５－７４４６３号では、負極にシリコンの単結晶を用いることで、サイクル特性が向上することを報告している。しかしながら、急速充放電用非水電解質電池の負極材として、シリコンにリチウムをドープさせようと試みると、ほとんどドープが起こらずにリチウムが析出してしまうことが分かった。そこで、本発明者らは、すでに不純物（ドーパント）を有するｐ型半導体、ｎ型半導体、ｐ－ｎ接合を有する半導体等の外来半導体について検討を行った結果、結晶の崩壊や微粉末化や脱落といった現象が起こらずにリチウムの吸蔵、放出がスムーズに進行することが分かった。さらに、この反応は約０．１Ｖという極めてリチウム電位に近い電位で進行し、理論容量に近い高容量が得られ、可逆性に優れることが分かった。

【００１４】また、該外来半導体は、電子伝導性の優れたものがリチウムとの合金化に適していることも分かった。特に電子伝導度が常温で$10^{-5}Scm^{-1}$以上、好ましくは、$1Scm^{-1}$以上である外来半導体が充放電特性に優れていることが分かった。つまり、リチウムとシリコンの合金は知られているものの、シリコン自身は元来真性半導体であり、そのままでは電子伝導性が低く、電池負極材料としての特性が悪かった。そのため、研究の対象になりにくい素材であったが、不純物をドーピングしたｐ型半導体、ｎ型半導体、ｐ－ｎ接合を有する半導体等の外来半導体、特にｐ型、ｎ型半導体においては不純物濃度が高く電子伝導性の良好なものが、また、不純物濃度が低くてもｐ－ｎ接合を有して順方向の電流に対して電気抵抗の低いものが、ともに負極活物質としてより充放電特性の優れたものであることを見い出し、本発明に至った。

【００１５】

【発明の実施の形態】ここで言う半導体材料としては、Ｓｉ，Ｇｅ，ＧａＡｓ，ＧａＰ，ＩｎＳｂ，ＧａＰ，ＳｉＣ等が挙げられ、それらのうちＳｉ，Ｇｅについては、特に優れた充放電特性が得られるので好ましいが、これらに限定されるものではない。また、その結晶系については、単結晶、多結晶、アモルファス等が挙げられ、それらのうち単結晶については、特に優れた充放電特性が得られるので好ましいが、これらに限定されるものではない。

【００１６】さらに、ここで言う不純物とは周期律表のすべての元素のうち、ドナー原子、アクセプター原子となり得るものであり、好ましくはＰ，Ａｌ，Ａｓ，Ｓｂ，Ｂ，Ｇａ，Ｉｎ，Ｓｎ等のＩＩＩｂ族、ＩＶｂ族、Ｖｂ族の元素であるが、これらに限定されるものではない。

【００１７】上記不純物のドーピング方法としては、ＣＺ法（チョクラルスキ法、または引き上げ法）、ＦＺ（フローティング・ゾーン法）、特にｐ－ｎ接合の作る場合は、合金法、拡散法、イオン注入法、エピタキシャル法等が挙げられるがこれらに限定されるものではない。

【００１８】不純物添加の濃度については、通常シリコン原子10^{7}個から10^{6}個にドナー原子あるいはアクセプター原子１個の割合であるが、好ましくは高濃度のドーピングが適しており、シリコン原子10^{4}個にドナー原子あるいはアクセプター原子１個の割合、またはそれ以上の高濃度であることが望ましい。

【００１９】本発明に用いる外来半導体は、厚みが０．１～５００μｍであるウエハー状の単板、もしくは平均粒子サイズ０．１～１００μｍである粉体が望ましい。所定の形状を得る上で、ウエハー状の単板を得るためにはダイヤモンドカッターが用いられ、また粉体を得るためには粉砕機や分級機が用いられる。粉体を得る場合、例えば乳鉢、ボールミル、サンドミル、振動ボールミル、遊星ボールミル、ジェットミル、カウンタージェットミル、旋回気流型ジェットミルや篩等が用いられる。粉砕時には水、あるいはヘキサン等の有機溶剤を共存させた湿式粉砕を用いることもできる。分級方法としては、特に限定はなく、篩や風力分級機などが乾式、湿式ともに必要に応じて用いられる。

【００２０】本発明に併せて用いる事ができる負極材料としては、リチウム金属、リチウム合金などや、リチウムイオンまたはリチウム金属を吸蔵放出できる焼成炭素質化合物やカルコゲン化合物、メチルリチウム等のリチウムを含有する有機化合物等が挙げられる。また、リチウム金属やリチウム合金、リチウムを含有する有機化合物を併用する事によって、本発明に用いる外来半導体にリチウムを電池内部で挿入する事も可能である。

【００２１】本発明の外来半導体を粉末として用いる場合、電極合剤として導電剤や結着剤やフィラー等を添加することができる。導電剤としては、電池性能に悪影響を及ぼさない電子伝導性材料であれば何でも良い。通常、天然黒鉛（鱗状黒鉛、鱗片状黒鉛、土状黒鉛など）、人造黒鉛、カーボンブラック、アセチレンブラック、ケッチェンブラック、カーボンウイスカー、炭素繊維や金属（銅、ニッケル、アルミニウム、銀、金など）粉、金属繊維、金属の蒸着物、導電性セラミックス材料等の導電性材料を１種またはそれらの混合物として含ませることができる。これらの中で、黒鉛とアセチレンブラックとケッチェンブラックの併用が望ましい。その添加量は１～５０重量％が好ましく、特に２～３０重量％が好ましい。

【００２２】結着剤としては、通常、テトラフルオロエチレン、ポリフッ化ビニリデン、ポリエチレン、ポリプロピレン、エチレンープロピレンジエンターポリマー（ＥＰＤＭ）、スルホン化ＥＰＤＭ、スチレンブタジエンゴム（ＳＢＲ）、フッ素ゴム、カルボメトキシセルロース等といった熱可塑性樹枝、ゴム弾性を有するポリマ

ー、多糖類等を１種または２種以上の混合物として用いることができる。また、多糖類の様にリチウムと反応する官能基を有する結着剤は、例えばメチル化するなどしてその官能基を失活させておくことが望ましい。その添加量としては、１～５０重量%が好ましく、特に２～３０重量%が好ましい。

【００２３】フィラーとしては、電池性能に悪影響を及ぼさない材料であれば何でも良い。通常、ポリプロピレン、ポリエチレン等のオレフィン系ポリマー、アエロジル、ゼオライト、ガラス、炭素等が用いられる。フィラーの添加量は０～３０重量%が好ましい。

【００２４】電極活物質の集電体としては、構成された電池において悪影響を及ぼさない電子伝導体であれば何でもよい。例えば、正極集電体の材料としては、アルミニウム、チタン、ステンレス鋼、ニッケル、焼成炭素、導電性高分子、導電性ガラス等の他に、接着性、導電性、耐酸化性向上の目的で、アルミニウムや銅等の表面をカーボン、ニッケル、チタンや銀等で処理した物を用いることができる。負極集電体の材料としては、銅、ステンレス鋼、ニッケル、アルミニウム、チタン、焼成炭素、導電性高分子、導電性ガラス、Ａｌ－Ｃｄ合金等の他に、接着性、導電性、耐酸化性向上の目的で、銅等の表面をカーボン、ニッケル、チタンや銀等で処理した物を用いることができる。これらの材料については表面を酸化処理することも可能である。これらの形状については、フォイル状の他、フィルム状、シート状、ネット状、パンチ又はエキスパンドされた形状、ラス体、多孔質体、発砲体、繊維群の形成体等が用いられる。厚みは特に限定はないが、１～５００μｍ程度のものが用いられる。

【００２５】この様にして得られるｐ型半導体、ｎ型半導体、ｐ－ｎ接合を有する半導体等の外来半導体を負極活物質として用いる。一方、正極活物質としては、MnO_2, MoO_3, V_2O_5, Li_xCoO_2, Li_xNiO_2, $Li_xMn_2O_4$, 等の金属酸化物や、TiS_2, MoS_2, $NbSe_3$ 等の金属カルコゲン化物、ポリアセン、ポリパラフェニレン、ポリピロール、ポリアニリン等のグラファイト層間化合物、及び導電性高分子等のアルカリ金属イオンや、アニオンを吸放出可能な各種の物質を利用することができる。

【００２６】特に本発明のｐ型半導体、ｎ型半導体、ｐ－ｎ接合を有する半導体等の外来半導体を負極活物質として用いる場合、高エネルギー密度という観点からV_2O_5, MnO_2, Li_xCoO_2, Li_xNiO_2, $Li_xMn_2O_4$ 等の３～４Ｖの電極電位を有するものが望ましい。特にLi_xCoO_2, Li_xNiO_2, $Li_xMn_2O_4$ 等のリチウム含有遷移金属酸化物が好ましい。

【００２７】また、電解質としては、例えば有機電解液、高分子固体電解質、無機固体電解質、溶融塩等を用いることができ、この中でも有機電解液を用いることが好ましい。この有機電解液の有機溶媒として、プロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、ジエチルカーボネート、ジメチルカーボネート、メチルエチルカーボネート、γーブチロラクトン等のエステル類や、テトラヒドロフラン、２－メチルテトラヒドロフラン等の置換テトラヒドロフラン、ジオキソラン、ジエチルエーテル、ジメトキシエタン、ジエトキシエタン、メトキシエトキシエタン等のエーテル類、ジメチルスルホキシド、スルホラン、メチルスルホラン、アセトニトリル、ギ酸メチル、酢酸メチル、Ｎ－メチルピロリドン、ジメチルフォルムアミド等が挙げられ、これらを単独又は混合溶媒として用いることができる。また支持電解質塩としては、$LiClO_4$、$LiPF_6$、$LiBF_4$、$LiAsF_6$、$LiCF_3SO_3$、$LiN(CF_3SO_2)_2$ 等が挙げられる。一方、高分子固体電解質としては、上記のような支持電解質塩をポリエチレンオキシドやその架橋体、ポリフォスファゼンやその架橋体等といったポリマーの中に溶かし込んだ物を用いることができる。さらに、Li_3N, ＬｉＩ等の無機固体電解質も使用可能である。つまり、リチウムイオン導伝性の非水電解質であればよい。

【００２８】セパレーターとしては、イオンの透過度が優れ、機械的強度のある絶縁性薄膜を用いることができる。耐有機溶剤性と疎水性からポリプロピレンやポリエチレンといったオレフィン系のポリマー、ガラス繊維、ポリフッ化ビニリデン、ポリテトラフルオロエチレン等からつくられたシート、微孔膜、不織布が用いられる。セパレーターの孔径は、一般に電池に用いられる範囲のものであり、例えば０．０１～１０μｍである。また、その厚みについても同様で、一般に電池に用いられる範囲のものであり、例えば５～３００μｍである。

【００２９】本発明の外来半導体に於いてウエハー状の板状の形状として用いる場合、集電をとる目的で集電体と活物質の間に導電性接着層を設けることもできる。導電性接着剤として通常、銀ペースト、カーボンペーストが用いられる。また、結晶の一部をニッケルメッキすることによって、ハンダや銀ロウのような溶融した金属による接合も可能である。また、その形状は、ダイヤモンドカッターやエッチング処理によって自由に加工することができる。

【００３０】この様な優れた充放電特性が得られる理由は必ずしも明確ではないが、以下のように考察される。すなわち、シリコン等の共有結合を有する結晶はリチウムとの合金が可能であり、その容量は大きいことが窺える。しかしながら、シリコン等の共有結合を有する結晶は半導体であるものの真性半導体であり、その常温での電気伝導度は低く充放電時の分極が比較的大きいのに対し、ｐ型半導体、ｎ型半導体、ｐ－ｎ接合を有する半導体等の外来半導体として、シリコン等の共有結合を有す

る結晶を用いると電子伝導度が向上し、容易にリチウムイオンを０価のリチウムとして吸蔵して電子を与えることができ、また吸蔵された０価のリチウムは電子を放出し、リチウムイオンとして放出される。つまり、結晶内部での電子の流れがリチウムイオンの吸蔵放出を容易にすると推定される。さらに、この結晶自身が共有結合を有し、その構造がダイヤモンドと同じ面心立方構造であるため非常に強固であり、リチウムの吸蔵放出に関わる膨脹収縮に追随し、活物質自身の微細化や脱落といったことが見られず、充放電の可逆性を向上しているものと考えられる。

【００３１】本発明の、ｐ型半導体、ｎ型半導体、ｐ－ｎ接合を有する半導体等の外来半導体を主構成物質とする負極活物質は、非水電解質中において金属リチウムに対し少なくとも０～２Ｖの範囲でリチウムイオンを吸蔵放出することができ、また半導体結晶が強固なことから、通常の合金に見られる充放電時の微細粉化や負極活物質の部分的な孤立化が抑えられ、このような負極活物質を電極材料として用いることにより、サイクル可能な充放電特性の優れた二次電池の負極として用いることができる。特に高濃度の不純物のドープや、ｐ－ｎ接合を有することにより、結晶内部での電子伝導性が向上することによって、シリコンとリチウムの合金化をスムーズにし、充放電のレート特性が向上する。さらに、負極電位がリチウム電位に近く低いため、電池としての電圧が高電圧となり、またその容量が大きいことから高エネルギー密度が達成される。

【００３２】

【実施例】以下、本発明の実施例について説明する。

（実施例１）拡散法により、シリコン原子10^4個にＰ原子１個の割合でドープしたｎ型半導体であるシリコン単結晶を（ａ）、シリコン原子10^4個にＢ原子１個の割合でドープしたｐ型半導体であるシリコン単結晶を（ｂ）、シリコン原子10^4個にＰ及びＢ原子１個の割合でドープし、ｐ－ｎ接合を形成した半導体であるシリコン単結晶を（ｃ）とする。厚さ０．３ｍｍ×縦５ｍｍ×横５ｍｍの大きさに切り出し、重量を測定した。この固有抵抗はｎ型半導体は３３Scm^{-1}、ｐ型半導体は２０Scm^{-1}であった。次に、縦１０ｍｍ×横１０ｍｍのニッケルメッシュ２枚で挟み込み、ワイヤーを取り付け試験電極とした。以下の操作は乾燥空気中で行い、材料はすべてあらかじめ十分に乾燥を行った後に用いた。適当な大きさの金属リチウムをニッケル板上に圧着したものを２個作製し、対極及び電位参照極とした。ビーカー中で$LiClO_4$を１ｍｏｌ／リットルの濃度に溶解したプロピレンカーボネート溶液を電解液とし、上記で作製した３個の電極、即ち試験電極、対極、電位参照極を電解液中に浸漬し、三端子セルとした。この単極性能試験セルを用いて充放電試験を行った。このセルに１ｍＡ電流を流し、電位参照極に対する試験極の電位が０．００～２．００Ｖの範囲について容量試験を行った。

（比較例１）不純物を含まない半導体としてシリコン単結晶（ｄ）を厚さ０．３ｍｍ×縦５ｍｍ×横５ｍｍの大きさに切り出し、重量を測定した。この固有抵抗は$10^{-6}Scm^{-1}$であった。これ以外は上記実施例１と同様にして単極性能試験セルを作製し同様の容量試験を行った。

【００３３】この様に作製した単極性能試験セルの容量試験を行った。シリコン単結晶（ａ）～（ｄ）を用いた単極性能試験セルをそれぞれのセル（Ａ）～（Ｄ）とする。セル（Ａ）～（Ｃ）に関してはリチウムの吸蔵放出が確認されたが、セル（Ｄ）についてはほとんどリチウムの吸蔵放出ができずリチウムの析出が観察された。このときの初期の容量と１０サイクル目の容量を表１に示した。この結果から明らかなように、本発明である不純物をドープした外来半導体を用いた負極については、充放電サイクル性に優れ、高容量であることが分かる。

【００３４】

【表１】

単極性能試験セル	１サイクル(Ah/g)		１０サイクル(Ah/g)	
	充電容量	放電容量	充電容量	放電容量
(A)	1．9	1．5	1．5	1．5
(B)	1．9	1．5	1．5	1．5
(C)	2．0	1．6	1．6	1．6
(D)	0．1	0．0	0．0	0．0

【００３５】（実施例２）実施例１で用いたシリコン単結晶（ａ），（ｂ）、ｎ型半導体としてシリコン原子10^4個にＰ原子１個の割合でドープしたシリコン多結晶を（ｅ）、ｐ型半導体としてシリコン原子１０４個にＢ原子１個の割合でドープしたシリコン多結晶を（ｆ）、について乳鉢で粉砕し、この負極活物質を用いて次のようにしてコイン型リチウム二次電池を試作した。負極活物質とアセチレンブラック及びポリテトラフルオロエチレン粉末とを重量比８５：１０：５で混合し、トルエンを加えて十分混練した。これをローラープレスにより厚み０．３ｍｍのシート状に成形した。次にこれを直径１６ｍｍの円形に打ち抜き、減圧下２００℃で１５時間熱処理して負極２を得た。負極２は負極集電体７の付いた負極缶５に圧着して用いた。

【００３６】正極１は、正極活物質として$LiCoO_2$とアセチレンブラック及びポリテトラフルオロエチレン粉末とを重量比８５：１０：５で混合し、トルエンを加

えて十分混練した。これをローラープレスにより厚み０．８mmのシート状に成形した。次にこれを直径１６mmの円形に打ち抜き、減圧下２００℃で１５時間熱処理して正極１を得た。正極１は正極集電体６の付いた正極缶４に圧着して用いた。　エチレンカーボネートとジエチルカーボネートとの体積比１：１の混合溶剤に$LiPF_6$を１mol／リットルの濃度に溶解した電解液を用い、セパレータ３にはポリプロピレン製微多孔膜を用いた。上記正極、負極、電解液及びセパレータを用いて直径２０mm、厚さ１．６mmのコイン型リチウム電池を作製した。このシリコン単結晶（a），（b）を用いた電池をそれぞれA１，Ｂ１とし、シリコン多結晶（e），（f）を用いた電池をそれぞれＥ１，Ｆ１とする。なお、図１に本発明のコイン型リチウム電池の断面図を示す。

【００３７】（比較例２）単結晶シリコンの代わりにアルミニウム粉末を用い、それ以外は実施例２と同様にして電池を作製した。得られた電池をＧ１とする。

【００３８】（実施例３）銅集電体上にアモルファスシリコンを０．１mmの厚さにコーティングしイオン注入法によりＰとＢをそれぞれ１立方センチメートル当たり10^{18}個注入したものを負極として用い、それ以外は実施例２と同様にして電池を作製した。得られた電池をＨ１，Ｉ１とする。

【００３９】（実施例４）単結晶シリコンの代わりに単結晶ゲルマニウム粉末を用い、エピタキシャル法によりゲルマニウム原子10^4個にＡｓ原子１個の割合でドープしたｎ型半導体であるゲルマニウム単結晶を（ｊ）、ゲルマニウム原子10^4個にＩｎ原子１個の割合でドープしたｐ型半導体であるゲルマニウム単結晶を（ｋ）とし、これらの単結晶を負極に用いた以外は実施例２と同様にして電池を作製した。得られた電池をＪ１，Ｋ１とする。

【００４０】このようにして作製した電池Ａ１，Ｂ１，Ｅ１，Ｆ１，Ｇ１，Ｈ１，Ｉ１，Ｊ１，Ｋ１を用いて充放電サイクル試験を行った。試験条件は、充電電流３mA、充電終止電圧４．２V、放電電流３mA、放電終止電圧３．０Vとした。これら作製した電池の充放電試験の結果を表２に示す。

【００４１】

【表２】

電池	１サイクル(mAh)		１０サイクル(mAh)	
	充電容量	放電容量	充電容量	放電容量
A１	６５	６３	６２	６２
Ｂ１	６４	６２	６２	６２
Ｅ１	６３	６１	５５	５４
Ｆ１	６３	６０	５５	５４
Ｇ１	６５	６２	３０	２８
Ｈ１	４６	４５	４４	４４
Ｉ１	４６	４５	４４	４４
Ｊ１	６５	６３	６２	６２
Ｋ１	６５	６３	６２	６２

【００４２】表１から分かるように本発明による電池Ａ１，Ｂ１，Ｅ１，Ｆ１，Ｈ１，Ｉ１，Ｊ１，Ｋ１は比較電池Ｇ１に比べて充放電特性に優れ、さらに１０サイクル後の容量減少が小さかった。また、Ａ１，Ｂ１とＥ１，Ｆ１の比較から、単結晶半導体のサイクル特性が、多結晶半導体よりも優れていることが分かる。この理由については明確ではないものの、次のように考えられる。多結晶半導体は、多くの小さな結晶の塊の集合であり、結晶と結晶の間には粒界が存在する。これらの材料にはがリチウムを吸蔵、放出するにあたって結晶の体積変化が生じる。つまり、この体積変化に伴って粒界部分に亀裂が入り、活物質の電子的孤立化、微粉末化が生じてサイクル劣化が起こると考えられる。アモルファスシリコンを用いたＨ１，Ｊ１については、若干容量が低下したものの、サイクル特性は優れている。また、シリコンとゲルマニウムの単結晶においてはその性能にほとんど差が見られなかった。

【００４３】実施例においては、外来半導体としてシリコン，ゲルマニウムについて挙げたが、同様の効果が他の外来半導体についても確認された。なお、本発明は上記実施例に記載された活物質の出発原料、製造方法、正極、負極、電解質、セパレータ及び電池形状などに限定されるものではない。

【００４４】

【発明の効果】本発明は上述の如く構成されているので、高電圧、高容量、高エネルギー密度で、優れた充放電サイクル特性を示し、安全性の高い非水電解質電池を提供できる。

【図面の簡単な説明】

【図１】本発明のコイン型リチウム電池の断面図である。

【符号の説明】

1	正極
2	負極
3	セパレータ
4	正極缶
5	負極缶
6	正極集電体
7	負極集電体
8	絶縁パッキング

【図１】